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The available invention concerns a procedure for the production of acrylic acid or Methacrylsäure.

Acrylic acid is an important basic chemical. Due to its very reactive double bond as well as the Säurefunktion it is suitable in particular as Monomeres for the production of polymers. From the manufactured quantity of acrylic acid monomers the larger part before the polymerization becomes - z. B. Adhesives, dispersions or lacquers - third. Only the smaller part manufactured acrylic acid monomers becomes direct - z. B. ?Superabsorbers? - polymerizes. While generally with the direct polymerization of the acrylic acid monomers of high purity are needed, the requirements are not so high to the purity of the acrylic acid, if this becomes before the polymerization third.

It is well-known the fact that acrylic acid can be manufactured by heterogeneously catalyzed gaseous phase oxidation by Propen with molecular oxygen on in the firm state of aggregation catalysts present at temperatures between 200 and 400 DEG C single-step or in two stages over Acrolein (see. z. B. DE-A-19 62,431, DE-A-29 43,707, DE-C-12 05,502, DE-A-195 08,558, EP-A-0 257,565, EP-A-0 253,409, DE-A-22 51,364, EP-A-0 117,146, GB-B-1 450,986 and EP-A-0 293,224). Here oxidic multi-component catalysts become z. B. on the basis of oxides of the elements molybdenum, bismuth and iron (in the 1. Stage) and/or. Molybdenum and vanadium (in the 2. Stage) assigned.

From DE-C-21 36,396 is well-known, the acrylic acid from with the catalytic oxidation of Propen and/or. Acrolein received reaction gases by counter current absorption with a mixture from approximately 75 Gew. - % Diphenylether and about 25 Gew. - To separate % Diphenyl. Further 49,780 the cooling of the hot reaction gas is well-known by partial evaporation of the solvent in a direct condenser (Quenchapparat) before the counter current absorption from DE-A-24. Problematic here as well as with further process steps the accumulation of solids is in the apparatuses, which reduces the plant availability. In accordance with DE-A-43 08,087 this solid accumulation can be reduced thereby by one the relatively nonpolar solvent mixture from Diphenylether and Diphenyl a polar solvent such as Dimethylphthalat in a quantity from 0,1 to 25 Gew. - % adds.

Apart from described above the absorption other well-known procedures a total condensation of acrylic acid plan the acrylic acid of containing reaction product into a high-boiling solvent mixture and the reaction water further developing with the catalytic oxidation. Develops an aqueous acrylic acid solution, which over distillation with a azeotropen means (see. DE-C-34 29 391, JP-A-1 124 766, JP-A-7 118 766, JP-A-7 118 966-R, JP-A-7 118 968-R, JP-A-7 241 885) oder über ein Extraktionsverfahren (vgl. DE-A-21 64 767, JP-A-5 81 40-039 und JP-A-4 80 91 013) weiter aufgearbeitet werden kann. In EP-A-0 551 111 wird das mittels katalytischer Gasphasenoxidation hergestellte Gemisch von Acrylsäure und Nebenprodukten mit Wasser in einem Absorptionsturm in Berührung gebracht und die erhaltene wässrige Lösung in Anwesenheit eines Lösungsmittels, das mit polaren Leichtesiedern wie Wasser oder Essigsäure ein Azeotrop bildet, destilliert. DE-C-23 23 328 beschreibt die Abtrennung von Acrylsäure aus einer wässrigen Butanol-Acrylsäure-Veresterungsablauge durch Extraktion mit einem speziellen Gemisch organischer Lösungsmittel.

With the procedures described above it is unfavorable that for the extraction or absorption an organic solvent is used, which is again separated in a further Verfahrensstufe like a rectification during high thermal load. Hierbei besteht die Gefahr einer Polymerisierung der Acrylsäure.

▲ top JP-A-07 082 210 beschreibt ein Verfahren zur Reinigung von Acrylsäure, die neben Acrylsäure Essigsäure, Propionsäure, Acrolein und Furfural enthält. With this procedure after addition by water a crystallization is accomplished in the vacuum, whereby after separation and washing the acrylic acid crystals a purity is reached of 99,6%. The Japanese patent 45-32417 reveals a procedure, with that an aqueous acrylic acid solution and/or. Methacrylsäurelösung, which contains additionally acetic acid and Propionsäure, is extracted with heptane or toluol and afterwards water is removed by distillation from the excerpt. In the next stage the remaining excerpt on -20 to -80 DEG C is cooled down, over a crystallization of acrylic acid and/or. To cause Methacrylsäure. The crystals are separated, and the mother liquor is reconducted the extraction process. In accordance with this patent specification is the use of an organic solution and/or. Extracting agent necessarily, since otherwise the solution, if it is cooled down, solidifies itself, without crystals fail. With this procedure it is unfavorable beside the additive of an organic solvent that for the separation by water a distillation must be accomplished. The Canadian patent 790,625 concerns a further purification process for raw acrylic acid by fractionated crystallization. In case of of Propionsäure as main pollution of the raw acrylic acid the temperature is not lowered under the peritektische temperature of the system acrylic acid Propionsäure, while in case of of acetic acid as main pollution the temperature is not lowered under the eutectic temperature of the system acrylic acid acetic acid. The acrylic acid used for crystallization is manufactured here in conventional procedures, for example by gaseous phase oxidation of Propen or Acrolein, and afterwards a prepurifying by conventional well-known procedures, z. B. Extraction, subjected. In accordance with the data of the patent specification the crystallization of the acrylic acid is preferably essentially accomplished in absence by water.

In EP-A-0 616,998 a procedure for the cleaning of acrylic acid is described by means of a combination of dynamic and static crystallization, whereby as charging product prepurified acrylic acid, for example distillative prepurified acrylic acid, is used.

It is common to the procedures described in the above documents that they require a prepurifying of the acrylic acid before the crystallization. Since during prepurifying usually organic solvents are used, which are again separated afterwards during high thermal load, the problem of an unwanted polymerization of the acrylic acid here always exists.

From EP-A-0 002,612, which concerns a procedure for the cleaning of acrylic acid available in aqueous solution by fractionated crystallization, the additive from salts is well-known to the acrylic acid solution, in order to break the eutectic open water acrylic acid, which is with 63% Volumengehalt acrylic acid.

EP-A-0 675,100 describes a procedure for the production alpha, beta - unsaturated C3-C6-Carbonsäuren, z. B. Methacrylsäure, by oxidative dehydrogenation of the appropriate saturated C3-C6-Carbonsäure followed by distillation or followed by fractionated distillation with following fusion crystallization, fractionated by fusion crystallization with.

The task of the available invention consisted of creating a procedure with acrylic acid or Methacrylsäure without complex Verfahrensstufen in high purity is received.

Surprisingly it was found that acrylic acid or Methacrylsäure from a gaseous product mixture, which is submitted of a condensation directly from the solution developing with the condensation it can be crystallized. In particular it was found that it requires for this no further cleaning stage and no additive of auxiliary materials.

Thus the invention concerns a procedure for the production of acrylic acid or Methacrylsäure through.

(A) Production of a gaseous product mixture, which essentially the composition of a reaction mixture of the catalytic gaseous phase oxidation of C3-/C4-Alkanen, - alkenes, - alkane oils and/or - Alkanalen and/or preliminary stages of it to acrylic acid or Methacrylsäure have, characterized through

(B) Condensation of the gaseous product mixture,

(C) Crystallization of the acrylic acid or Methacrylsäure from the solution received in stage (B),

(D) Separation of the received crystals from the mother liquor and

(E) Feedback at least one part of the mother liquor from stage (D) in stage (B).

In a preferential execution form the condensation is accomplished in stage (B) in a column. Further preferential execution forms of the invention result from the following description, the Unteransprüchen, the figure and the example.

With the procedure according to invention the acrylic acid or Methacrylsäure without further intermediate or cleaning stages and without additive of auxiliary materials from the solution one crystallizes directly and directly, which develops with the condensation of the product mixture. This product mixture has essentially the composition of a reaction product developing with the catalytic gaseous phase oxidation to the acid.

The only figure points a preferential remark example to the execution of the procedure according to invention.

(A) gradates

In stage (A) a gaseous product mixture is manufactured, that essentially the composition of a reaction mixture of the catalytic gaseous phase oxidation of C3 and/or. C4-Alkanen, - alkenes, - alkane oils and/or - Alkanalen and/or preliminary stages of it to acrylic acid or Methacrylsäure have. The gaseous product mixture becomes particularly favourable by catalytic gaseous phase oxidation of Propen, propane, Acrolein, third. - Butanol, Isobuten, ISO butane, Isobutyraldehyd, Methacrolein, ISO butter acid or methyl third. - more butylether manufactured. As parent compounds all preliminary stages of the C3-/C4-Verbindungen specified above can be used, with which the actual C3-/C4-Ausgangsverbindung forms only intermediately during the gaseous phase oxidation. For the production of the Methacrylsäure methyl third is exemplarily mentioned. - more butylether or ISO butter acid. Both acrylic acid and Methacrylsäure can directly from propane and/or. ISO butane to be manufactured.

The catalytic gaseous phase reaction is particularly favourable from Propen and/or Acrolein to acrylic acid with molecular oxygen in well-known procedures, in particular like it in the block letters specified above is described. Preferably becomes here at temperatures between 200 and 450 DEG C and if necessary. increased pressure worked. Preferably oxidic multi-component catalysts on the basis of the oxides of molybdenum, bismuth and iron in the 1 become as heterogeneous catalysts. Stage (oxidation from Propen to Acrolein) and the oxides of molybdenum and vanadium in the 2. Stage (oxidation from Acrolein to acrylic acid) assigned. These conversions are accomplished for example single-step or in two stages. Wird Propan als Ausgangsstoff verwendet, so kann dieses zu einem Propen-/Propan-Gemisch umgesetzt werden durch: catalytic oxide hydrogenation, like z. B. in Catalysis Today 24 (1995), 307-313 or US-A-5 510,558 described; by homogeneous oxide hydrogenation, like z. B. in CN-A-1 105,352 described; or by catalytic dehydrogenation, like z. B. in EP-A-0 253,409, DE-A-195 08,558, EP-A-0 293,224 or EP-A-0 117,146 described. Suitable prop. EN/propane mixtures are also Raffineriepropen (70% Propen and 30% propane) or Crackerpropen (95% Propen and 5% propane). In principle prop. EN/propane mixtures can like the o. g. with oxygen or air or a mixture from oxygen and nitrogen of each composition to Acrolein and acrylic acid to be oxidized. With employment of a prop. EN/propane mixture propane works as dilution gas and/or reactant. A suitable procedure is also in EP-B-0 608,838 is described, with the propane as reactant directly to acrylic acid converted.

The conversion from Propen to acrylic acid is strongly exothermic. The reaction gas, that beside the Edukten and products favourable-proves an inert dilution gas, z. B. Circle gas (see below), atmospheric nitrogen, one or more satisfied C1-C6-Kohlenwasserstoffe, in particular methane and/or propane, and/or water vapour contains, can therefore only a small part of the heat of reaction take up. Although the kind of the used reactors is subject actually to no restriction, bank of tubes heat exchangers are usually used, which are filled with the oxidation catalyst, since with these the predominant part of the warmth freed with the reaction can be exhausted by convection and radiation to the cooled tube sheets.

With the catalytic gaseous phase oxidation pure acrylic acid does not become, but a gaseous mixture receive, which can contain essentially not converted Acrolein and/or Propen, water vapour, Carbon monoxide, Kohlendioxid, Stickstoff, Propan, Sauerstoff, Essigsäure, Propionsäure formaldehyde, further aldehydes and maleic acid anhydride beside the acrylic acid as Nebenkompenten. Usually the reaction product mixture, in each case related to the entire reaction mixture, contains 1 to 30 Gew. - % acrylic acid, 0.05 to 1 Gew. - % Propen and 0.05 to 1 Gew. - % Acrolein, 0.05 to 10 Gew. - % oxygen, 0.05 to 2 Gew. - % acetic acid, 0.01 to 2 Gew. - % Propionsäure, 0.05 to 1 Gew. - % formaldehyde, 0.05 to 2 Gew. - % aldehydes, 0.01 to 0.5 Gew. - % maleic acid anhydride and 20 to 98 Gew. - %, preferably 50 to 98 Gew. - %, inert dilution gases. As inert dilution gases is in particular satisfied C1-C6-Kohlenwasserstoffe, like 0 to 90 Gew. - % methane and/or propane, beside it 1 to 30 Gew. - % water vapour, 0.05 to 15 Gew. - % carbon monoxides and 0 to 90 Gew. - % nitrogen, in each case related to 100 Gew. - % dilution gas, contain.

Die Methacrylsäure kann analog zu Acrylsäure durch katalytische Gasphasenreaktion von C4-Ausgangsverbindungen mit molekularem Sauerstoff hergestellt werden. Besonders vorteilhaft ist die Methacrylsäure, z. B. by catalytic gaseous phase oxidation of Isobuten, ISO butane, third. - Butanol, ISO Butyraldehyd, Methacrolein or methyl third. - more butylether available. As catalysts likewise transition-metallic mixing oxide catalysts (z become. B. Mo, V, W and/or Fe) use, whereby the conversion is accomplished for example single-step or multi-level. Particularly suitable procedures are such, with which the production on the basis of Methacrolein takes place, in particular if the Methacrolein by gaseous phase-catalytic oxidation of third. - Butanol, ISO butane or Isobuten or by conversion by formaldehyde with Propionaldehyd in accordance with EP-B-0 092,097 or EP-B-0 058,927 are produced. Thus also the possibility exists in two stages of manufacturing Methacrylsäure by (1) condensation of

Propionaldehyd with formaldehyde (in presence of a secondary amine as catalyst) to Methacrolein and (2) following oxidation of the Methacroleins to Methacrylsäure. A further suitable procedure is in EP-B-0 608,838 to be described, with ISO butane than reactant directly to Methacrylsäure be converted can.

Just like with the production of the acrylic acid pure Methacrylsäure does not become, but a gaseous mixture receive, which can contain of the Methacrylsäure beside as Nebenkomponenten essentially not converted Methacrolein and/or water vapour, Carbon monoxide, Kohlendioxid, Stickstoff, Sauerstoff, Essigsäure, Propionsäure, further aldehydes and maleic acid anhydride. The procedure according to invention is used in particular if the reaction mixture, 0.02 to 2 Gew. - % Methacrolein related to the entire reaction mixture and otherwise essentially the same appropriate components as with the production of the acrylic acid contains.

(B) gradates

In stage (B) the reaction product of a condensation, in particular of a portion aluminum or a total condensation, received in stage (A), is submitted, whereby a solution will receive.

Die Kondensation wird vorzugsweise in einer Kolonne durchgeführt. Here a column with separate-effective installations, in particular with packings, is used filling materials and/or soils, preferably bubble trays, sieve inserts, valve trays and/or dual flow soils. The condensable components of the gaseous product mixture from stage (A) are condensed fractionated by cooling. There the gas mixture due to the impurities and dilution gases a heavy simmering he, a central simmering he and a light they the parliamentary group as well as not-condensable components contains, can at the column in the appropriate places one or more Seitenabzüge be intended. Contrary to a usual condensation a condensation in a column thus already makes an isolating possible into the individual components. Suitable columns cover at least cooling device, for which all usual heat-transfer agents or heat exchangers, with which the warmth formed with the condensation is dissipated indirectly (externally), are suitable. Are preferential bank of tubes heat exchangers, plate-type heat exchangers and air coolers. Suitable cooling agents are air with the appropriate air cooler and coolants, in particular water, with other cooling devices. Only if one cooling device is intended, then this is inserted at the head of the column, in which the light they the parliamentary group is condensed. There the acrylic acid and/or. Methacrylsäure haltige gas mixture several parliamentary groups contains, is it appropriate to insert several cooling devices in different sections the column z. B. a cooling device in the lower section of the column to the Auskondensation of the heavy they the parliamentary group and a cooling device at the head of the column to the Auskondensation of the light they the parliamentary group. The parliamentary group with the acrylic acid and/or. Methacrylsäure is taken off in the middle part of the column over one or more Seitenabzüge. In the column the available, pressure depends on the quantity of condensable components and does not amount to preferably 0.5-5 bar absolute pressure, in particular 0.8-3 bar absolute pressure. The exact operating conditions for the column, like temperature and pressure guidance, circuit and arrangement of the cooling device (EN), arrangement of the Seitenabzugs/the Seitenabzüge for taking the acryl and/or. off Methacrylsäure, choice of the column height and the column diameter, number and the distance of the separate-effective installations/soils in the column or kind of the separate-effective column installations, can be determined by the specialist in the context of specializedusual attempts as a function of the task of separation. In a preferential execution form the hot gas mixture is cooled down directly or indirectly before the Auskondensation. To prefer it is in the case of the direct cooling that the gas mixture is cooled down with the help of the heavy they the parliamentary group condensed from the gas mixture. In the other case an auxiliary material is registered into the procedure, which must be regenerated however again. Machine can this precooling in the sump range of the column integrated (with or without column installations) or separately from the column in its own apparatus, z. B. a Gaskühler, a Quench or a Flashtopf take place. In a particularly preferred arrangement of the invention the condensation of the gaseous reaction mixture runs off in a column as follows, whereby the column can be arranged into different sections, in which the following different process engineering tasks is solved:

1. Sump range

Cooling of the hot gas mixture

Within the sump range the hot gas mixture is introduced and cooled down. This can over indirect cooling, z. B. Heat exchangers, or direct cooling also in the next section of the column of condensed heavy they the parliamentary group as cooling agent take place.

2. First cooling circle

Condensation of the heavy they the parliamentary group

Within the range of the first cooling circle the condensation warmth becomes external over the first cooling circle by means of a heat exchanger with z. B. Water as cooling agent is cooled exhausted, as condensed heavy they the parliamentary group from the column is exhausted, by means of the heat exchanger and a part of the cooled, condensed heavy they the parliamentary group of the column is reconducted, during the other part, usually less than 1 Gew. - % related to 100 Gew. - % condensate in the Seitenabzug is removed. Die rückgeführte, kondensierte Schwertsiederfraktion wird im Gegenstrom zum aufsteigenden Gas geführt.

3. First cooling circle to Seitenabzug

Heavy they the enrichment

Between first cooling circle and the Seitenabzug a distillative enrichment and Auskondensation of the heavy they the parliamentary group from upward gas flow the led the against the current take place to the first cooling circle.

4. Seitenabzug

Take off from the acid

Über den Seitenabzug wird die Acrylsäure bzw. Methacrylsäure abgeführt.

5. Seitenabzug bis zweiter Kühlkreis

Anreicherung der Mittelsiederfraktion

Im Bereich zwischen dem Seitenabzug und dem zweiten Kühlkreis erfolgt die Anreicherung der Mittelsiederfraktion aus dem im Gegenstrom nach oben geführten Gasstrom, wobei die Mittelsiederfraktion zum Seitenabzug hin angereichert wird.

6. Zweiter Kühlkreis

Condensation of the light they the parliamentary group

In the range of the second cooling circle the condensation of the light they the parliamentary group from upward gas flow the led the against the current takes place. The condensation-warm becomes external over the second cooling circle by means of a heat exchanger with z. B. Water as cooling agent exhausted, as condensed light they the parliamentary group is withdrawn, cooled and reconduted a part of the cooled, condensed light they the parliamentary group of the column, while the other part is removed. The not condensed components, with which it preferably concerns nitrogen, Carbon monoxide, Kohlendioxid, Sauerstoff, Methan, Propan and Propen, could be taken off from the head of the column.

Besides the condensation can take place in usual procedures single or multi-stage, whereby the kind is not subject to the condensation of special restriction. Favourable way is accomplished the condensation with a direct condenser, whereby condensate already produced is brought with the hot gaseous reaction product in contact. Als Apparate für die Kondensation eignen sich insbesondere Sprühwäscher, Venturiwäscher, Blasensäulen oder Apparate mit berieselten Oberflächen.

Die durch Partial- oder Totalkondensation des Reaktionsprodukts aus Stufe (a) erhaltene Mischung, insbesondere das Kondensat der Mittelsiederfraktion bei Kondensation in einer Kolonne, enthält vorzugsweise 60 bis 99,5 Gew.-% Acrylsäure bzw. Methacrylsäure, 0, 1 to 40 Gew. - % water, beside it 0.1 to 15 Gew. - % impurities, in particular, in each case related to 100 Gew. - % condensate, 0.01 to 5 Gew. - % (Meth) acrolein, 0.05 to 5 Gew. - % acetic acid, 0.01 to 5 Gew. - % Propionsäure, 0.01 to 5 Gew. - % formaldehyde, 0.01 to 5 Gew. - % further aldehydes and 0.01 to 5 Gew. - % maleic acid. Particularly with the condensation a mixture is kept preferred, which 93 to 98 Gew. - % acrylic acid and/or. Methacrylsäure, 1 to 5 Gew. - % water, beside it 0.5 to 5 Gew. - % impurities, in particular, in each case related to 100 Gew. - % condensate, 0.01 to 3 Gew. - % Acrolein and/or. Methacrolein, 0.1 to 3 Gew. - % acetic acid, 0.01 to 3 Gew. - % Propionsäure, 0.01 to 3 Gew. - % formaldehyde, 0.01 to 3 Gew. - % further aldehydes and 0.01 to 3 Gew. - % maleic acid contains.

(C) gradates

In stage (C) becomes the solution received in stage (B), the acrylic acid and/or. Methacrylsäure contains, crystallized. Thus the solution received in the condensation stage is supplied directly to the crystallization. Here without additive of a solvent, in particular without additive of an organic solvent, one works. The used crystallization procedure is not subject to restriction. The crystallization can be accomplished continuously or intermittent, single-step or multi-level. Preferably the crystallization takes place single-step. In another preferential execution form of the invention the crystallization than fractionated crystallization is accomplished. Usually all stages with fractionated crystallization, which a Kristallisat produces, become, which is purer than the supplied aqueous acrylic acid solution and/or. Methacrylsäurelösung, cleaning stages mentioned and all other stages drift stages mentioned. Multi-level procedures are appropriately operated here after the countercurrent principle, with which after the crystallization in each stage the Kristallisat is separated from the mother liquor and this Kristallisat of the respective stage with the next higher degree of purity is supplied, while the crystallization arrears of the respective stage with the next lower degree of purity are supplied.

Favourable way lies the temperature of the solution during the crystallization between +5 DEG C and +14 DEG C, in particular between 8 DEG C and 12 DEG C. The solid content in the crystallizer lies favourable-proves between 0 and 80 g/100 g, preferentially between 15 and 35 g Feststoff/100 G.

In a favourable arrangement of the invention the crystallization takes place via cooling of apparatus walls or via evaporation of the solution in the vacuum. With the crystallization by cooling the warmth is dissipated over Kratzkühler, which are connected with an agitating boiler or a container without agitator. The circulation of the crystal suspension is ensured here by a pump. Besides also the possibility exists of exhausting the warmth over the wall of an agitating boiler with wind-usual agitator. A further preferential execution form with the cooling crystallization is the use of cooling disk crystals, like it z. B. of the company Gouda (Holland) to be manufactured. With a further suitable variant for crystallization by cooling the warmth is dissipated over conventional heat-transfer agents (bank of tubes or disk heat carrier prefers). These apparatuses do not possess a device contrary to Kratzkühlern, agitating boilers with wind-usual agitators or cooling crystal wafers for the avoidance of crystal layers on the warm-transferring surfaces. In the enterprise if a condition is reached, with which the heat transfer resistance takes a too high value by crystal layer formation, the change-over takes place on a second apparatus. While the period of operation of the second apparatus the first apparatus is regenerated (preferably by melting of the crystal layer or flushing the apparatus with insatiated solution). In the second apparatus if a too high heat transfer resistance is reached, one switches the first apparatus around etc. This variant can be operated also with more than two apparatuses in the change. In addition the crystallization can take place via a conventional evaporation of the solution in the vacuum. In a further favourable execution of the invention the crystallization in apparatuses, in which the crystals grow up in the crystallization apparatus at cooled surfaces, takes place D. h. are fixed in the apparatus (z. B. Layer crystallization procedure of the companies Sulzer Chemtech (Switzerland) or static crystallization procedure of the companies BEFS PROKEM (France)).

(D) gradates

In stage (D) the acrylic acid crystals received in stage (C) become and/or. Methacrylsäurekristalle separated from the mother liquor. For the case of the layer crystallization or the static crystallization the separation of the crystals from the mother liquor can take place in the crystallization apparatus, since the crystals are fixed in the apparatus and the mother liquor can be removed by discharging letting from the apparatus. Die Entfernung der Kristalle aus dem Kristallisationsapparat erfolgt durch Aufschmelzen der Kristalle und nachfolgendes Abfließenlassen der Schmelze. Für den Fall der Suspensionskristallisation eignen sich alle bekannten Verfahren der Fest-Flüssig-Trennung. In einer bevorzugten Ausführungsform der Erfindung werden die Kristalle durch Filtrieren und/oder Zentrifugieren von der Mutterlauge abgetrennt. Vorteilhafterweise wird dem Filtrieren oder Zentrifugieren eine Voreindickung der Suspension, zum Beispiel durch Hydrozyklon(e), vorgeschaltet. Zum Zentrifugieren eignen sich alle bekannten Zentrifugen, die diskontinuierlich oder kontinuierlich arbeiten. Thrust centrifuges are used most favourably, which can be single or multi-stage operated. Besides also snail filter centrifuges or snail discharge centrifuges (decanter) are suitable. A filtration effected favourable-proves those by means of Filternut, intermittent or continuously, with or without agitator, or by means of band filters to be operated. Generally filtering under pressure or in the vacuum can take place.

During and/or after the fixed liquid separation further process steps can for the increase of the purity of the crystals and/or. the crystal cake to be planned. In a particularly favourable arrangement of the invention follow after separating the crystals from the mother liquor in or multi-level washing and/or sweating of the crystals or the crystal cake. When washing is the washing liquid quantity be suitable-proves between 0 and 500 g Waschflüssigkeit/100 g Kristallisat, preferably between 30 and 200 g Waschflüssigkeit/100 g Kristallisat. The used washing liquid is not subject to a restriction. Favourable way is washed however with pure product, D. h. with a liquid, the acrylic acid and/or. Methacrylsäure contains, whose purity is higher than the crystal cake which can be washed. Besides also a laundry with water is possible. Washing can take place in for this usual apparatuses.

Favourable way washing columns, in which the separation of the mother liquor and washing take place in an apparatus, become centrifuges, which can be single or multi-stage operated, or Filternut or band filters use. Washing can be single or multi-stage accomplished on centrifuges or band filters. Here the washing liquid the against the current can be led to the crystal cake.

When sweating it concerns local melting of contaminated ranges. Favourable way amounts to the sweating quantity between 0 and 100 g Kristallinat/100 g Kristallinat before sweating, melted, preferably between 5 and 35 g Kristallinat/100 g Kristallinat melted. The execution of sweating on centrifuges or band filters is particularly preferential. Also the execution of a combination of washing and sweating in an apparatus can be suitable.

The acrylic acid crystals and/or. Methacrylsäurekristalle after the fixed liquid separation and if necessary. represent the cleaned acid from the procedure to further washing and/or sweating. The purity of the received crystals amounts to usually 97 to 99.99 Gew. - % acrylic acid and/or. Methacrylsäure, in particular 98.5 to 99.9 Gew. - % acrylic acid and/or. Methacrylsäure. According to invention the crystals manufactured in the procedure contain only more completely small quantities of impurities, like acetic acid, maleic acid or aldehydes.

If desired, the cleaned acid can according to well-known methods third or according to well-known methods to be further cleaned.

(E) gradates

Into stage (E) is led back the mother liquor from stage (D), staying after separation of the crystals, at least partly directly into the condensation stage (B). The portion of the led back mother liquor lies between 0 and 100 Gew. - %, in particular 80 to 100 Gew. - %, preferably he amounts to 100 Gew. - %.

The figure points a preferential remark example to the execution of the procedure according to invention. By way of line 2 and compressor 3 air is supplied to the synthesis reactors 4 and 5. The reactor 4 over the line 9 of the compressor 6 consolidated circle gas, which essentially consists of nitrogen, carbon monoxides and not converted Edukten, becomes additional as well as from the line 1 coming Propen and/or. Isobuten supplied. In the synthesis reactor 4 the first stage of the two-stage gaseous phase oxidation takes place, i.e. the oxidation of Propen and/or. Isobuten to the appropriate Acrolein. In the synthesis reactor 5 then the Acrolein to the appropriate acid one oxidizes. Here develops a gaseous product mixture, which contains further, impurities above mentioned beside the acid. This is supplied to the condenser 8 by way of the line 7, in which it is cooled down and condensed. The condenser 8 is designed in the figure as column. The not-condensed part of the product mixture is exhausted over the line 9, described above of the one part as circle gas, as, led back the reactor 4 and the other part, preferably 50% total value of current of the line 9, when exhaust gas from the plant is exhausted over the line 10. The condensed heavy they the parliamentary group is exhausted over the line 18, while the condensed light they the parliamentary group is exhausted over line 19. The condensed central they the parliamentary group, those the largest part of the acrylic acid and/or. Methacrylsäure contains, over the line 11 (Seitenabzug) of the crystallization device 12 is supplied, in which the crystallization is accomplished. The mother liquor from the crystallization is supplied to a suitable apparatus 14 together with the Kristallinat over line 13 for fixed liquid separation, whereby over the line 15 the Kristallinat is exhausted and over the line 16 the mother liquor. At least one part of the mother liquor is led across the line 17 into the condenser 8, supplied preferably within the range of the Seitenabzugs (line 11), and thus the condensation again. Thus over the line 15 the cleaned raw acid is exhausted.

By the feedback the available invention makes a high yield up to 99,5% for the mother liquor possible into the condensation stage. Das erfindungsgemäße Verfahren eignet sich insbesondere zur Abtrennung von Acrylsäure bzw. Methacrylsäure aus solchen Reaktionsgasgemischen, die signifikante Mengen an Wasserdampf enthalten.

Das erfindungsgemäße Verfahren bietet gegenüber den bisher bekannten Verfahren weiterhin den Vorteil, dass nach Kondensation des bei der Gasphasenoxidation entstehenden Produktgemischs direkt aus der bei der Kondensation entstehenden Lösung durch Kristallisation eine Rohsäure mit sehr guter Qualität erhalten wird. Beim Einsatz einer Kristallisation mit mehr als einer Reinigungsstufe kann direkt eine Reinsäure erzeugt werden, wobei anders als in den oben genannten Schriften, kanadisches Patent 790 625, JP-A-0 07 082 210-A und EP-A-0 616 998 keine Vorreinigung erfolgen muss.

Ein weiterer wichtiger Vorteil des erfindungsgemäßen Verfahrens ist, dass das Verfahren relativ kalt durchgeführt wird, d. h. the main stream at acrylic acid is led directly across condensation and crystallization as product of the process. Da anders als im Stand der Technik kein Hilfsstoff zugesetzt wird und somit keine hohe thermische Belastung (insbesondere bei hohen Acrylsäuregehalten) zur Abtrennung dieses Hilfsstoffes erforderlich ist, werden Polymerisationsprobleme und der Einsatz von Prozessstabilisatoren, wie sie im Stand der Technik hierbei auftreten, verringert. In addition thereby also the Fouling is avoided or reduced. It is surprising that it is possible to be able to crystallize by gaseous phase oxidation and condensation received acrylic acid solutions or Methacrylsäurelösungen directly and that hereby products will receive to very high purity. In particular was it surprising that this is possible with aqueous condensates also.

The invention is described on the basis the following example, which represents a preferential execution form of the invention, more near.

Example

From the reaction stage (A) the following mixture with a temperature of 270 DEG C by catalytic gaseous phase oxidation from Propen was received.

Table 1
EMI21.1

EMI22.1

The mixture (10,931 g/h) was supplied to the condensation stage (B). As condensation apparatus a Bodenkolonne with 27 bubble trays was used. The temperature in the column sump amounted to 100 DEG C. The condensation warmth was exhausted over heat-transfer agents at the soils 1 and 27. At the head of the column Phenothiazin was admitted as stabilizer. At the soil 27 a river was taken off from the following composition from 425 g/h:

Table 2
EMI23.1

At the column sump a river was taken off from the following composition from 2 g/h:

Table 3
EMI24.1

The exhaust gas had the following composition:

Table 4
EMI25.1

The exhaust gas from the Kondensationskolonne was led back into the reaction (60 Gew. - %) and/or. from the process (40 Gew. - %) removed.

Am Boden 11 wurde ein flüssiger Strom von 4657 g/h und 84,5 DEG C aus der Kolonne abgezogen, der dann kristallisiert wurde. Dieser Strom hatte folgende Zusammensetzung:

Tabelle 5
EMI26.1

Subsequently, the mixture in 10 an l agitating container with spiral agitator, coming from the soil 11, one crystallized. The crystallization warmth was exhausted over the double coat of the container. The Gleichgewichtstemperatur of the solution amounted to 4.8 DEG C. The suspension produced with the crystallization (30 g Feststoff/100 g suspension) was separated on a centrifuge with 2000 rpm (centrifuge diameter 250 mm) and a centrifuge time from 1 min into crystals and mother liquor. The crystals (1281 g/h) were washed afterwards with melted Kristallisat (296 g/h) 1 min long with 2000 rpm.

The mother liquor (3376 g/h) was gone back together with the washing liquid into the Kondensationskolonne on soil 10. The analysis of the crystals resulted in the following composition:

Table 6
EMI27.1

EMI28.1

As evident from table, the procedure according to invention makes the production of highly pure acrylic acid for 6 possible.



Result Page

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1. Procedure for the production of acrylic acid or Methacrylsäure through:

(A) Production of a gaseous product mixture, which essentially the composition of a reaction mixture of the catalytic gaseous phase oxidation of C3-/C4-Alkanen, - alkenes, - alkane oils and/or - Alkanalen and/or preliminary stages of it to acrylic acid or Methacrylsäure have, characterized through

(B) Condensation of the gaseous product mixture,

(C) Crystallization of the acrylic acid or Methacrylsäure from the solution received in stage (B),

(D) Separation of the received crystals from the mother liquor and

(E) Feedback at least one part of the mother liquor from stage (D) in stage (B).

2. Procedure according to requirement 1, by the fact characterized that in stage (A) the gaseous product mixture by catalytic gaseous phase oxidation of Propen, propane, Acrolein, third. - Butanol, Isobuten, ISO butane, Isobutyraldehyd, Methacrolein, ISO butter acid or methyl third. - one manufactures more butylether.

3. Procedure according to requirement 1 or 2, by the fact characterized that the condensation is accomplished in stage (B) in a column with separate-effective installations.

4. Procedure according to requirement 3, by the fact characterized that with the condensation the solution, which in stage (C) is crystallized, when the central they the parliamentary group is withdrawn.

5. Procedure after one of the preceding requirements, by the fact characterized that the crystallization is accomplished in stage (C) single-step or multi-level.

6. Procedure after one of the preceding requirements, by the fact characterized that the temperature of the solution lies during the crystallization in stage (C) between +5 DEG C and +14 DEG C.

7. Procedure after one of the preceding requirements, by the fact characterized that with the crystallization in stage (C) the warmth by cooling of apparatus walls or by evaporation of the solution in the vacuum is exhausted.

8. Procedure after one of the preceding requirements, by the fact characterized that the crystals in stage (D) by filtering and/or centrifugation are separated from the mother liquor.

9. Procedure after one of the preceding requirements, by the fact characterized that the crystals separated in stage (D) at least to washing and/or sweating are submitted.

10. Procedure after one of the preceding requirements, by the fact characterized that in stage (E) between 0 and 100 Gew. - %, preferably 100 Gew. - %, the mother liquor from stage (D) into the stage (B) to be led back.